

ROTATIONAL EXCITATION OF HYDROGEN MOLECULES BY COLLISIONS WITH HYDROGEN ATOMS

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ABSTRACT

Rate constants for rotational excitation of hydrogen molecules by collisions with hydrogen atoms have been obtained from quantum-mechanical calculations for kinetic temperatures between 100 and 5000 K. These calculations involve the rigid-rotator approximation, but other possible sources of error should be small. The calculations indicate that the early values of Nishimura are larger than accurate rigid-rotator values by about a factor of 20 or more.

Subject headings: interstellar: molecules — molecular processes

One of the fundamental parameters needed for understanding the energetics of the interstellar gas is the rate at which rotational motion of hydrogen molecules is excited by collisions with hydrogen atoms. Rate coefficients for this purpose have often been taken (see, e.g., Spitzer 1978) from the work of Nishimura (1968), who obtained them from a rigid-rotator distorted wave calculation with the modified wavenumber approximation and a Morse-type potential (Takayanagi and Nishimura 1960). More sophisticated theoretical treatment is now possible, and it is interesting to try to calculate more accurate rate coefficients. To this end, Elitzur and Watson (1978) have recently analyzed rigid-rotator calculations by Chu and Dalgarno (1975) and by McGuire and Krüger (1975), and have reached the conclusion that they lead to rate coefficients typically lower than Nishimura's by about a factor of 3 to 6. However, their study can be improved on two counts. First, while the scattering calculations of Chu and Dalgarno and of McGuire and Krüger are more sophisticated than the earlier work of Nishimura, they are still based on hybrid potential energy surfaces of less than state-of-the-art accuracy. The hybrid surface of Chu and Dalgarno is based on the vibrational average of a surface of Porter and Karplus (1964) at close range and on the interaction potential of Dalgarno, Henry, and Roberts (1966) at long range. The hybrid surface of McGuire and Krüger is based on the isotropic approximation of Gengenbach, Hahn, and Toennies (1975) and on the vibrational average of the leading anisotropic term in the Porter-Karplus potential. Second, both of these more recent calculations were limited to the lowest few rotational levels and to a few collision energies, and, to obtain rate constants for the range of rotational levels and kinetic temperatures of astrophysical interest, Elitzur and Watson have performed extensive interpolation and extrapolation

based on a model of collisional energy transfer whose validity has not been convincingly demonstrated. In the present *Letter*, we report more refined rigid-rotator calculations for this system for a range of rotational levels and collision energies. Our results are smaller than the values given by Nishimura by about a factor of 20 or more.

The calculation of collision cross sections can be divided into two separate problems: the determination of the intermolecular forces, i.e., the potential energy surface; and the computation of the collision dynamics resulting from these forces. It is possible, in principle, to obtain the intermolecular potential by solving the electronic Schrödinger equation; and because it has only three electrons, the H_2 potential energy surface has been the subject of numerous electronic structure calculations (Truhlar and Wyatt 1977). Most of these have focused on the region of the surface relevant to the hydrogen atom exchange reaction and have provided little information relevant to nonreactive energy transfer collisions. However, the recent, definitive study of this system by Siegbahn and Liu (1978) has provided accurate values for the potential over a large portion of the surface. The computed points have been fitted (Truhlar and Horowitz 1978) to an analytic form, and this form is used for the present scattering calculations. We note that 248 of the 267 calculated points used for this fit are for interaction energies in the range 0.13–3.5 eV. Thus, since rotational excitation in this system is dominated by repulsive interactions near the classical turning point for radial motion, we expect the surface to be most reliable for calculations in about the same range of relative translational energies. The most important collision energies for the rates reported here are generally in this range, although the threshold for the $0 \rightarrow 2$ excitation is only 0.06 eV. Thus for low rotational quantum numbers and low temperatures it

would be desirable to know the surface better for small interaction energies.

Previous calculations on $\text{H} + \text{H}_2$ rotational excitation and the effects of various approximations on the results are reviewed elsewhere (Truhlar and Wyatt 1977). In the present study, the hydrogen molecule is treated as a rigid rotator, with the internuclear distance r fixed at its equilibrium value r_e . The interaction then depends on the distance R of the hydrogen atom from the center of mass of H_2 and on the angle θ between the H_2 and H_2 -to- H axes. For quantum scattering calculations it is convenient to expand the angle dependence of the potential in Legendre polynomials,

$$V(R, \theta) = \sum_L V_L(R) P_L(\cos \theta). \quad (1)$$

The radial coefficients $V_L(R)$ were obtained by numerical quadrature of

$$V_L(R) = \frac{2L+1}{2} \int_{-1}^1 d(\cos \theta) V(R, \theta) P_L(\cos \theta) \quad (2)$$

for a set of distances $R = 1.0$ (0.2) 15.0 Bohr radii. Legendre terms through $L = 18$ were retained in the calculation. Polynomial interpolation (Green 1977) was used to obtain continuous radial functions from the $V_L(R_i)$.

Scattering calculations in the present *Letter* employed the approximate coupled states formalism, the same method as used by McGuire and Krüger (1975). This approximation is known to be quite accurate for other, similar molecular systems, giving cross sections generally within 20% of exact, close coupling values; similar accuracy (average error 27%) was documented for H_2 -H by comparing with close coupling calculations for representative cases. Calculations were performed separately for para- H_2 (even rotational levels) and ortho- H_2 (odd levels), since these are not interconverted in nonreactive collisions. For para- H_2 calculations were done at 37 total energies, and for ortho- H_2 they were done at 39 total energies; in both cases the energies extended from threshold to 25,000 cm^{-1} . Rotational basis sets were large enough to ensure convergence to within a few percent of the infinite basis set limit for the dominant cross sections; as a general rule two closed channels were retained. Rotational energies were computed assuming a rotation constant, $B_0 = 60 \text{ cm}^{-1}$, with no correction for centrifugal distortion. The coupled equations were solved by standard numerical techniques with tolerances chosen to reduce this source of error in the cross sections to generally less than 1%. The resulting cross sections for the dominant transitions are plotted in Figure 1 as a function of collision energy.

Rate constants were obtained by numerically integrating the cross sections over Boltzmann distributions for kinetic temperatures between 100 and 5000 K. From comparison of different algorithms, the numerical integration is thought to be accurate to better than about 5%. Results are given in Table 1. Having obtained the rates as a function of temperature, we can use the Tolman interpretation of the activation energy (Tru-

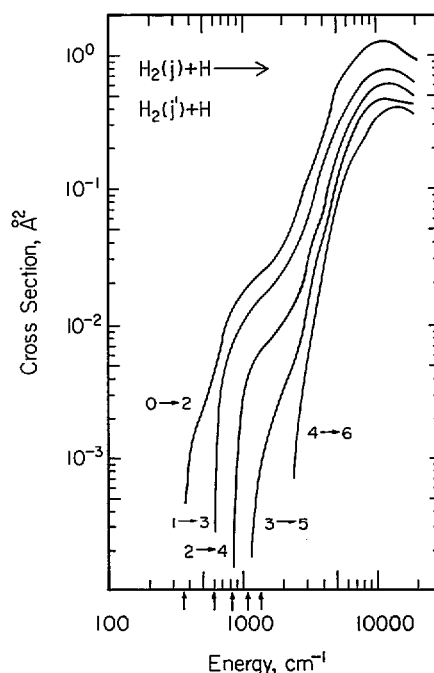


FIG. 1.—Excitation cross sections for the dominant transitions as a function of translational kinetic energy. Arrows on the abscissa indicate threshold energies.

lar 1978) to estimate the average relative translational energies for systems undergoing transitions. Using the rates at 300 and 3000 K yields values of 0.17–0.38 eV for the activation energies E_a for $j \rightarrow j+2$ transitions. The average relative translational energies for systems undergoing transitions are $E_a + 3kT/2$; for 300–3000 K, the range of these energies for $j \rightarrow j+2$ transitions is 0.14–0.77 eV. Thus except for low j at 100 K the surface is probably known well enough in the most important energy region.

It is believed that the largest uncertainties in the values in Table 1 are those arising from the potential energy surface and the rigid-rotator approximation. The error due to the potential energy surface is hard to estimate. A definitive assessment will have to await calculation of a more accurate potential energy surface or a detailed analysis of sensitivity of the rate coefficients to variations of the potential energy surface. However, the fact that an accurate potential energy surface, such as used here, leads to smaller rotational excitation cross sections than the Porter-Karplus one, and other surfaces considered, can be understood on the basis of the Legendre coefficients of the interaction potential (Choi and Tang 1975; Truhlar and Horowitz 1978).

In principle, rather than fix the H_2 internuclear distance at its equilibrium value r_e , it is more correct to average the interaction over the H_2 ground-state vibrational motion, as was done by Chu and Dalgarno. Another error is introduced by ignoring the possibility of collisionally exciting higher vibrational levels, even though the rate of vibrational excitation is typically several orders of magnitude slower than rotational

TABLE 1
 H₂-H COLLISIONAL EXCITATION RATES*

$j \rightarrow j'$	TEMPERATURE (K)					
	100	300	500	1000	3000	5000
0→2.....	1.0(-15)	9.7(-14)	3.6(-13)	2.1(-12)	3.6(-11)	8.2(-11)
1→3.....	7.5(-17)	4.4(-14)	2.0(-13)	1.2(-12)	2.0(-11)	4.9(-11)
2→4.....	1.8(-18)	9.8(-15)	6.5(-14)	5.6(-13)	1.4(-11)	3.6(-11)
3→5.....	8.0(-21)	7.5(-16)	1.1(-14)	2.4(-13)	9.7(-12)	2.7(-11)
4→6.....	1.3(-22)	5.1(-17)	1.8(-15)	1.1(-13)	7.0(-12)	2.0(-11)
5→7.....	4.8(-24)	2.8(-17)	9.1(-16)	6.2(-14)	5.2(-12)	1.6(-11)
6→8.....	6.6(-26)	6.1(-18)	3.8(-16)	3.5(-14)	3.7(-12)	1.2(-11)
7→9.....	2.6(-29)	6.7(-19)	1.2(-16)	2.0(-14)	2.6(-12)	9.0(-12)
0→4.....	1.1(-21)	4.4(-16)	8.6(-15)	1.2(-13)	2.1(-12)	6.2(-12)
1→5.....	4.4(-25)	1.0(-17)	3.7(-16)	9.3(-15)	7.3(-13)	3.1(-12)
2→6.....	5.0(-29)	2.9(-19)	4.4(-17)	3.3(-15)	4.0(-13)	2.0(-12)
3→7.....	9.7(-33)	2.1(-21)	1.0(-18)	5.4(-16)	2.3(-13)	1.3(-12)
0→6.....	2.8(-36)	4.0(-22)	2.9(-19)	1.9(-16)	1.2(-13)	6.3(-13)
1→7.....	1.6(-37)	9.8(-24)	1.2(-20)	3.0(-17)	4.0(-14)	2.6(-13)

* In units of cm³ s⁻¹; number in parentheses is power of 10.

excitation at the lowest collision energies considered here. The importance of vibrational effects would be expected to increase with collision energy or kinetic temperature, and eventually the hydrogen exchange reaction also becomes important. For the commonly used potential energy surface of Porter and Karplus (1964), the rigid-rotator approximation with $r = r_e$ has been tested. For that surface, Wolken, Miller, and Karplus (1972) found that the rigid-rotator cross section for the 0→2 excitation at a collision energy of 0.25 eV is about 20% lower when computed with the potential for $r = r_e$ than when computed with the vibrationally averaged potential. However, Schatz and Kuppermann (1976) found that fully converged vibrational-rotational close coupling, including reactive channels, for the nonreactive 0→2 transition for the Porter-Karplus surface led to excellent agreement with the vibrationally averaged results of both Wolken *et al.* and Choi and Tang (1975) at all relative translational energies up to 0.4 eV. Thus, for the Porter-Karplus surface, the error in the rigid-rotator approximation with the potential evaluated for $r = r_e$ seems to be only about 20% as compared with a calculation in

which vibrational effects are included completely. But after the present calculations were completed, Walker and Stechel (1979) made converged vibrational-rotational calculations of the nonreactive 0→2 cross sections for the same potential surface as used here and found results an order of magnitude larger than the present results for relative translational energies 0.18–0.33 eV. Thus the effect of vibration-rotation coupling is much larger for the present potential energy surface than for the Porter-Karplus surface. This may be in part a consequence of the much smaller rotational excitation cross sections for the present surface. It therefore seems that for use in applications, the present rigid-rotator rates should be considered as a lower bound to the exact results.

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